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Reporting Strange and Unique Behavior of 4CB Liquid Crystal using Logger Pro

Mathew C. Doran 1, MedaelleSeide 1, Dipti Sharma (PhD) 2*
1 Undergraduate student, Emmanuel College, Boston, MA 02115 USA
2 Supervisor, Emmanuel College, Boston, MA 02115 USA,
**Corresponding Author: Dr. Dipti Sharma*

ABSTRACT
This paper reports the unique behavior of 4-Butyl-4-Cyanobiphenyl (4CB) Liquid Crystal (LC) using Logger Pro. Two bulk samples, 4-Butyl-4-Cyanobiphenyl (4CB) and 4-Hexyl-Cyanobiphenyl (6CB) were used to run in a Differential Scanning Calorimetry (DSC) instrument to find their phase behavior and phase transitions appeared in heating and cooling. It is found that 4CB shows two unique behaviors in heating and two unique behaviors in cooling when it is heated from -40 °C to 80 °C and then cooled from 80 °C to -40 °C. The 4CB doesn't show Nematic phase in heating at all but shows two glass transition states whereas 6CB shows a typical behavior of LCs in heating with Nematic phase. On cooling, 4CB shows the presence of Nematic and double crystallization whereas 6CB shows single crystallization. This strange behavior of 4CB can be explained in terms of spring theory taking place in between C-C bonds that are in the tail of 4CB.

KEYWORDS: *Crystalline, Nematic, Isotropic, glassy, phase transitions, states of matter, 4CB, 6CB, Liquid Crystal, Temperature, Specific heat capacity, Thermodynamics, DSC, Physics, Chemistry, Material Science.*

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I. INTRODUCTION

Liquid Crystals (LCs) have been the material of interest of research for hundreds of years because of their unique properties of having multiple states. In 1888, Friedrich Reinitzer discovered liquid crystals by melting cholesteryl benzoate. Reinitzer recognized its properties by observing the phase changes that occur with the heat flow. Liquid crystals typically have 4 states, the crystalline, smectic, nematic, and isotropic that occur at certain temperatures when LCs are heated. Compared to other materials, LCs can move like liquids, but it has a molecular structure of a crystalline solid that is why it is called Liquid Crystal. [1-2]

One of the most important types of LC is thermotropic LC as they show types of states as temperature changes. In other words, thermotropic LCs are anisotropic liquid molecules that possess a phase with crystalline solid and liquid characteristics, which are dependent on the temperature. The most common thermotropic LC family is Alkyl Cyanobiphenyl (nCB) that has a tail made of C-C bonds. In this family, as the number (n) of carbon in the tail changes, the size of the member changes and hence they show multiple types of phases. The nCB family is made of one cyano group, two phenyl groups attached with a carbon chain as alkyl chain as a tail. [3-4] The typical states seen in them are Crystalline (K), Nematic (N) and Isotropic (I) but some may also have Smectic state that appears before Nematic state while they are heated.

The Crystalline (K) state is a long range ordered solid state that shows a very organized and rigid structure. In the Nematic (N) state, the molecules aren't in a set pattern, and they are partially organized or partially ordered but as an average they follow the vertical axis. They show an opaque gel-like structure in Nematic state. The molecules are arranged similarly to those in the Smectic (Sm) state, except they are more organized and denser than Nematic and show grouped alignment if they appear in LCs. Whereas, in the Isotopic (I) state, the molecules are-- completely disorganized and follow the liquid structure of molecules. The states of LCs can be detected or studied using calorimetric technique using Differential Scanning Calorimeter (DSC). [5-6] In DSC, heat flow is measured as a function of temperature to detect any change in the phase of LCs or any material that shows phase change. [6-13] LCs absorb thermal energy and shows endothermic peaks in heating for their phase transitions whereas they show release of heat as exothermic peaks when they are cooled in DSC. [8-14]

In this paper, the details of 4-Butyl-4-Cyanobiphenyl (4CB) are reported. The 4CB is a molecule with a four-carbon chain attached to the cyano biphenyl group which is the youngest and smallest LC in the Alkyl - Cyanobiphenyl (nCB) LC family. The detailed results of 4CB are compared with 4-Hexyl-Cyanobiphenyl (6CB), the other family member of nCB. The 6CB LC has six carbons in the tail with the same cyano biphenyl group. In addition, 6CB shows typical type of phase transitions as nCB shows but 4CB doesn't show that typical

behavior. The 4CB liquid crystal diverges from the expected pattern being youngest member in the family of nCB. [12-14]

We are interested in knowing details of 4CB to understand its strange behavior physically, chemically, and materially using DSC and Logger Pro. The 4CB undergoes to Crystalline and Isotropic phases in heating and skips Nematic whereas it shows Nematic in cooling after Isotropic and then goes to multiple Crystallization. More details can be seen in the results section of the paper and explanation can be seen in the discussion section. No such type of study has been found on 4CB in the literature yet.

When an object gets heated to a particular range of temperature, some materials go to glass transition and show a stretchy or rubbery behavior. They develop a more rubber-like structure. Glass transition is an important property for amorphous and semi-crystalline materials. It occurs within a temperature range when materials change from hard to fragile, and finally soft. The different states of the material help determine its real-world applications. [14-15] No study has been found on Liquid Crystals that shows presence of glass transition in liquid crystals, but we have found strange glassy appearance in 4CB and are reporting it here in detail.

II. THEORY AND EXPERIMENTS

Liquid crystals show thermodynamic properties when they are heated and cooled. They undergo from one state to another state based on types of liquid crystals. Thermodynamic details of LCs can be found by running them in Differential Scanning Calorimetry (DSC). DSC plots graphs of the material as heat flow versus temperature to show how states of material change. The heat flow given to the material can be described in the given equation as shown below where Q is heat, m is mass, Cp is specific heat capacity ΔT is change in temperature.

$$Q = m*Cp*\Delta T \quad — 1$$

The first derivative can be taken to equation 1 to find heat flow (dQ/dt) as a function of heating rate (dT/dt) that can be seen in equation 2.

$$dQ/dt = m*Cp*dT/dt \quad — 2$$

Enthalpy (ΔH) of the transitions can be found by taking the area under the peak and that can be found by integration graph plotted for Cp versus T as shown in the equation 3.

$$\Delta H = \int Cp*dT = (1/m) \int (dQ/dt)*dt \quad — 3$$

LCs are made up of organic compounds and contain C-C and C-H bonds. 4CB and 6CB have tails made with C-C and C-H bonds. [10] These bonds behave like spring and show spring theory in terms of spring constant (k) and spring potential energy (Ue) that can be seen in the equation 4 where F is force applied to the bond, x is the extension due to applied force, F. The Ue is the stored elastic potential energy in the bond and kt is the total spring constant when springs from 1-n are attached in series combination.

$k = F/x$ — 4 (a) and $U_e = ½ kx^2$ — 4(b)

$1/kt = 1/k1 + 1/k2 + \ldots 1/kn$ — 4(c)

Differential Scanning Calorimetric (DSC) Technique has been drawing attention of researchers and experimentalists for decades to study types of material, their thermal behavior, phase changes and types of states they have. In this experimental study, we tested 4-Butyl-4-Cyanobiphenyl (4CB) in detail in a DSC instrument called MDSC 2920 for heating and cooling where small amount of 4CB was heated from -40 °C to 80 °C and then cooled from 80 °C to -40 °C. The DSC results of 4CB were then compared with DSC results of 4-Hexyl-Cyanobiphenyl (6CB). It is found that 6CB shows a large down (endothermic) peak for Crystalline to Nematic and a small down (endothermic) peak for Nematic to Isotropic phase transitions on heating. On Cooling 6CB shows a small up (exothermic) peak for Isotropic to Nematic and then a large up (exothermic) peak for Nematic to Crystalline phase transitions on Cooling. This is a normal trend of peaks in heating and cooling for nCB liquid crystals. But 4CB has something missing and something new. The 4CB shows two strange things on its heating. When 4CB is heated in DSC from -40 °C to 80 °C, it shows a large down (endothermic) peak as Crystalline to Isotropic phase transition and No Peak for Nematic to Isotropic transition. **Nematic State in 4CB is Absent on Heating**!This is the first strange thing found in 4CB on heating. The other strange thing found in heating of 4CB is **Appearance of two steps on heating before Crystalline to Isotropic peak.** This type of steps found in DSC represents another type of transition that is called "Glass Transition". So, **4CB shows Glass Transition on Heating** that no liquid crystal in nCB shows or found yet. On the other side, on cooling, 4CB shows a small up (exothermic) peak for Isotropic to Nematic phase transition and then a large up (exothermic) but double peak as Nematic to Crystalline phase transition. That means **4CB shows Presence of Nematic State in Cooling Only but not in Heating. It also shows Double Crystallization in Cooling instead of single Crystallization.**

All experiments were repeated in DSC for 4CB to check the reproduction of results. The results were found reproducible. The DSC instrument was calibrated every time before the start of experiments. The respective heat flow of 4CB and 6CB was recorded as a function of temperature for heating and cooling in DSC. All environmental and experimental conditions were kept identical to make a good comparison of parameters studied for this paper.

After collecting DSC data for 4CB and 6CB, Logger Pro was used to plot graphs and analyze these data. The sample and data of 4CB was analyzed in detail to find reasons for why 4CB is showing strange behavior.

III. MOLECULAR STRUCTURE

The molecular weight of 4CB (C16H15N) and 6CB (C19H21N) are 235.33 g/mol and 263.4 g/mol respectively. The molecular structure of 4CB and 6CB contains two benzene rings and one cyano group with a tail of C-C and C-H groups. The 4CB has four C-C bonds in its tail whereas 6CB has six C-C bonds in its tail. The 2D molecular structure of 4CB can be seen in Figure 1(a) that shows a tail is made of C4H9 and Figure 1(b) has a zigzag structure with four folds.

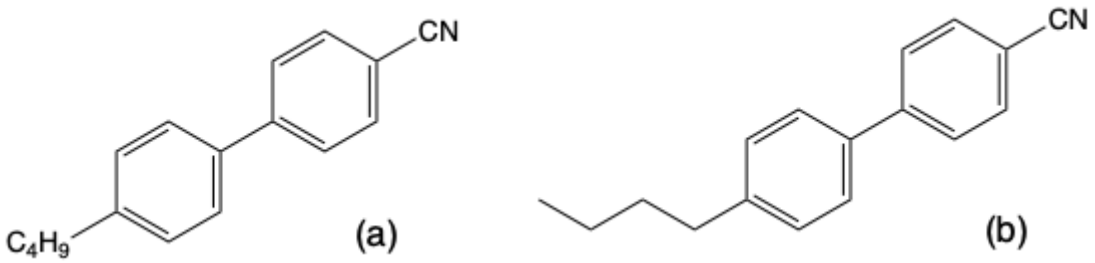

Figure 1 (a) 2D molecular structure of 4CB liquid crystal, **(b)** 2D molecular structure of 4CB liquid crystal showing two benzene and one cyanogroup with the full length of its carbon tail.

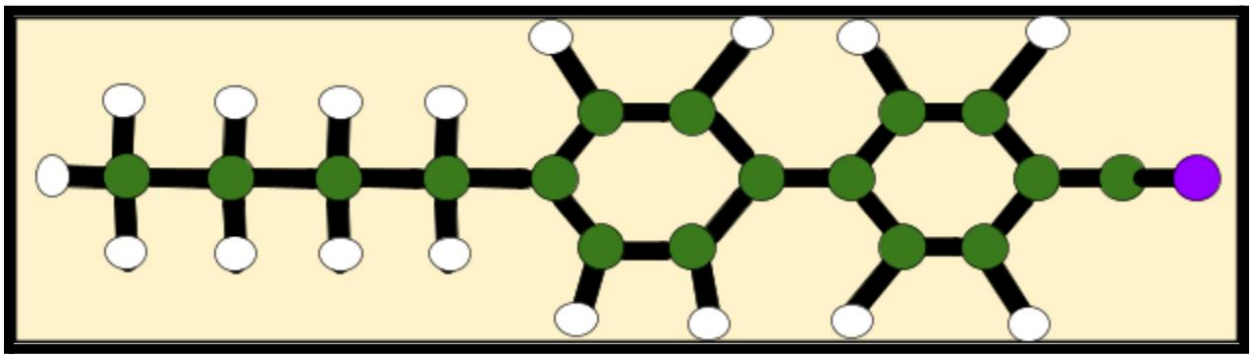

Figure 2. The 3D molecular structure of the 4CB LC showing the 4-carbon tail made of C-C bonds.

More details of the molecular structure of 4CB can be seen in its 3D molecular structure as shown in Figure 2. It can be seen how C-C and C-H bonds are attached to each other.

IV. RESULTS

(a) Strange Behavior of 4CB

Detailed DSC results of 4CB can be seen inFigure 3 that shows heat and cool of 4CB liquid crystal using DSC. On heating, 4CB shows a big endothermic peak as absorption of thermal energy as T_{KI} at 50.10 °C representing change of state of molecules from crystalline to isotropic state skipping nematic state. The flat line before and after this peak represents solid and liquid states. The transition peaks show where these two states mix at equilibrium at T_{KI}. On cooling, two exothermic were observed and they represent a change of state from isotropic to nematic as T_{IN} at 14.34 °C, and then from nematic to crystalline as T_{NK}. The interesting thing found in cooling is that 4CB shows presence of Nematic state in cooling but missed nematic in heating. Another interesting thing found in cooling is that 4CB shows multiple crystallization in cooling as double crystallization as two peaks in crystallization exothermic peaks as T_{NK1}, T_{NK2} at -11.47 °C and -13.78 °C.

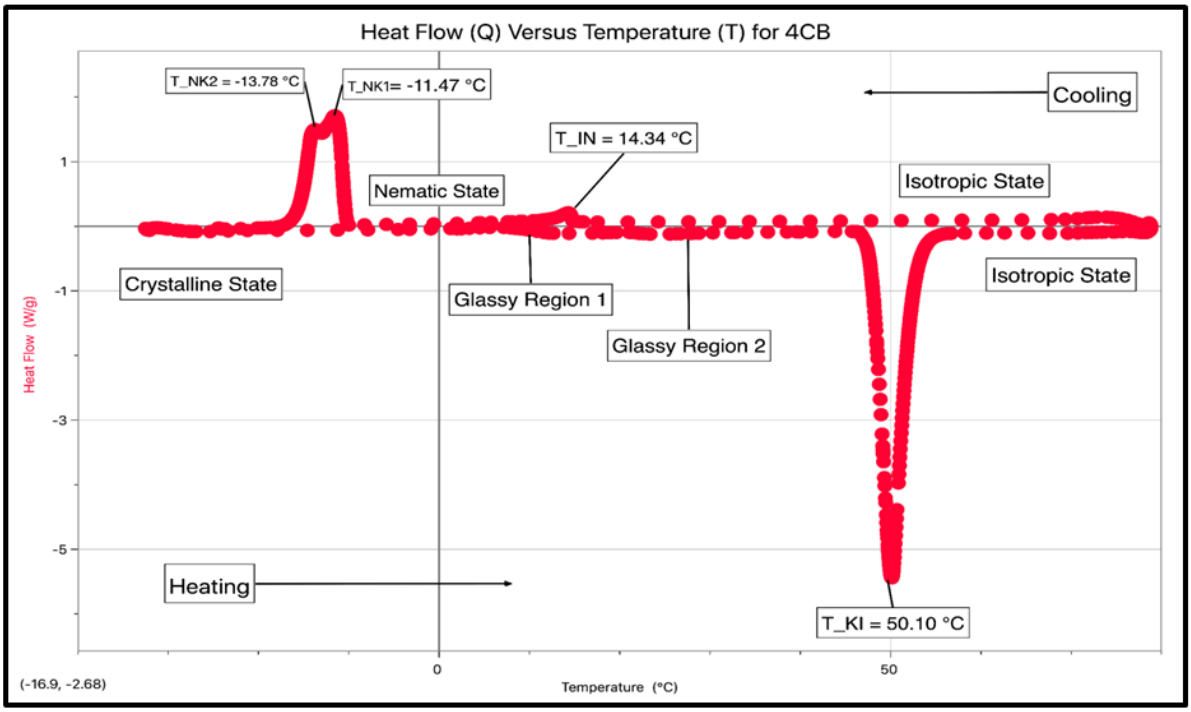

Figure 3. Heat flow Vs temperature plot of the heating Crystalline (K) to Isotropic (I) phase transition and the cooling Isotropic to Nematic (N) to crystalline phase transitions of 4CB liquid crystal.

Figure 4 displays the "typical" transition behavior of the next even member of the nCB family that is 6CB. The 6CB shows a typical trend of behavior of phase transitions in heating and cooling as nCB LCs shows. On heating, the 6CB shows a large endothermic peak for crystalline to nematic as T_{KN} and then a small endothermic peak for nematic to isotropic transition as T_{NI}. On cooling, 6CB shows both transitions coming back as nematic and crystalline from isotropic transitions. The 4CB doesn't follow the same trend as 6CB or as other nCB family members and show some missing and strange behavior on heating and cooling.

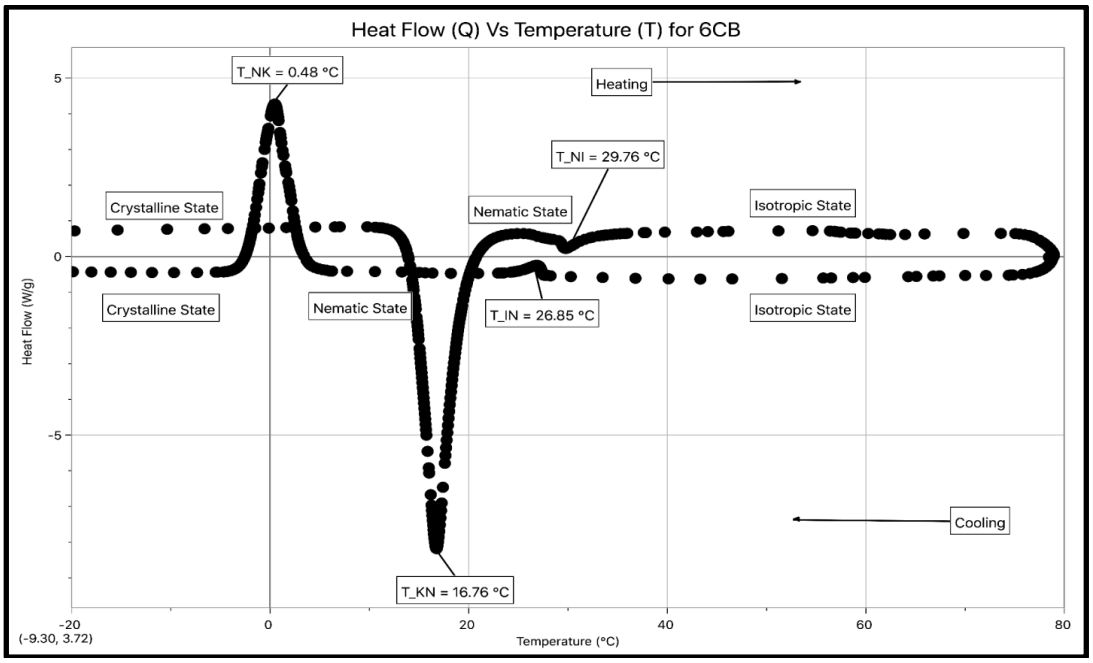

Figure 4. Heat flow Vs Temperature plot for K-N and N-I phase transitions for the heating and cooling of 6CB liquid crystals.

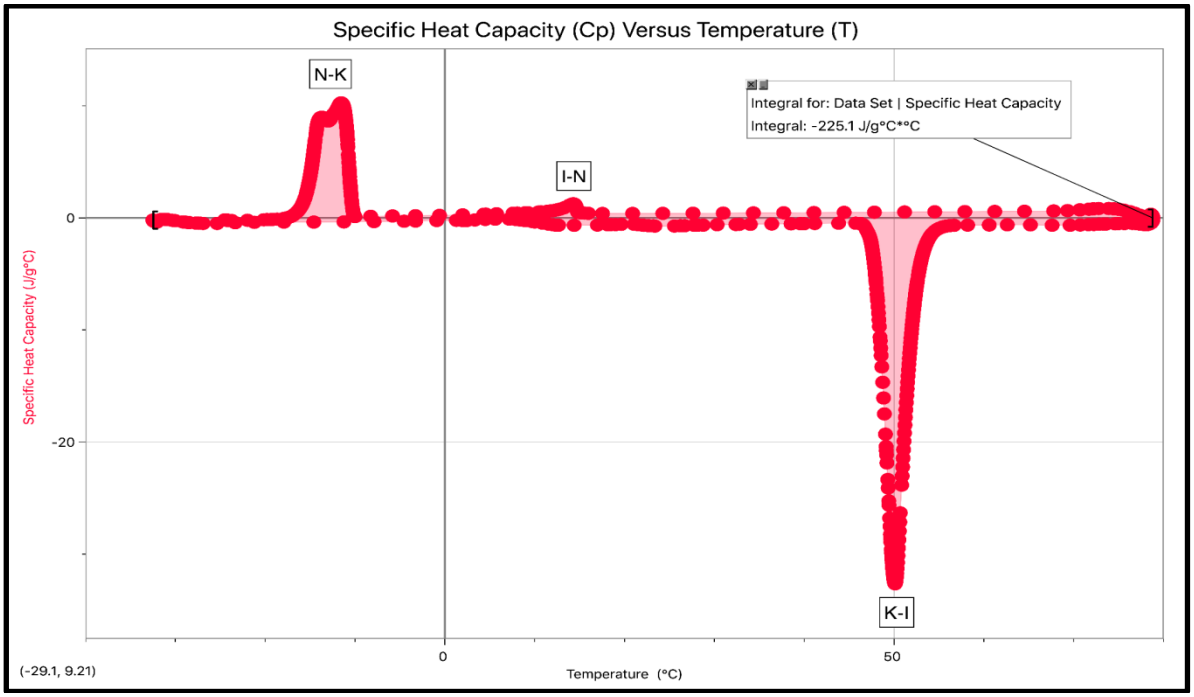

Figure 5. Specific heat capacity (Cp) Vs temperature (T) plot for 4CB liquid crystal for heating and cooling. The pink color shows the integral between heating and cooling.

The DSC data is then plotted as a specific heat capacity versus temperature plot for 4CB to see more detailed facts of 4CB and shown in Figure 5. InFigure 5 the shaded area shows the integral of the heating and cooling phase transition curve that represents the amount of energy withheld by the 4CB molecule throughout the phase transitions which represent the change in its internal energy during heating and cooling. The total internal energy change of the 4CB is found as 225.1 J/g, as seen in Figure 5.

(b) Presence of Glass Transition in 4CB

While 4CB is heated from -40 °C to 80 °C in DSC, it is found that before getting a large endothermic peak in heating, 4CB shows some more strange behavior and it can be seen in Figure 3. When Figure 3 is zoomed in to see those features in detail, it is observed that there are two steps present in heating. This indicates that 4CB goes to a glassy state from its crystalline state before it melts. These steps can be seen in detail in Figure 6 as two steps as glassy state 1 at T_{g1} and glassy state 2 at T_{g2}. It also means that 4CB goes to two different glassy states that makes 4CB as stretchy and rubbery for a short moment until it goes to T_{KI} transition and melts completely as liquid.

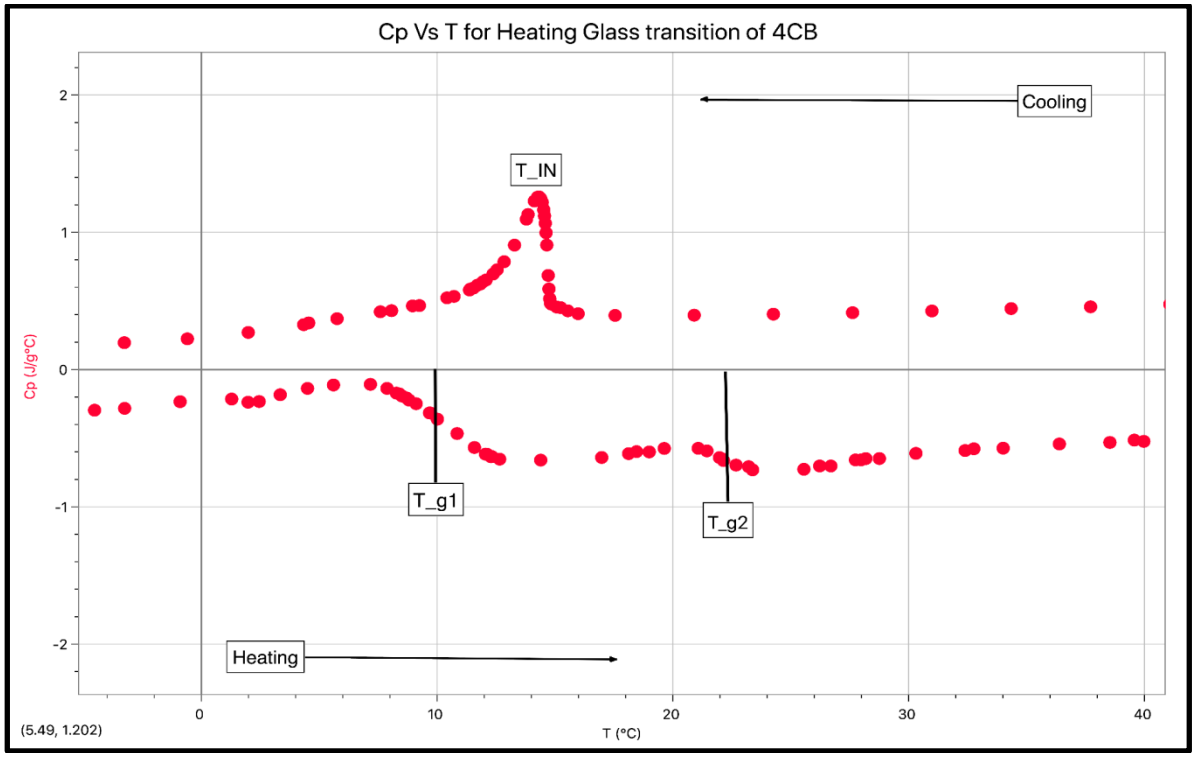

Figure 6. Specific heat capacity Vs Temperature plot for the observed Two glass transitions in heating for 4CB.

(c) Enthalpy of Transitions in 4CB

The enthalpies of the phase transitions that appear as a peak either in heating or cooling for 4CB is calculated as peak integration that shows how much heat and thermal energy is absorbed or released by these peaks during heating and cooling. Figure 7 shows the thermal energy absorbed in the endothermic peak by K-I transition of 4CB in heating which comes as 106.6 J/g.

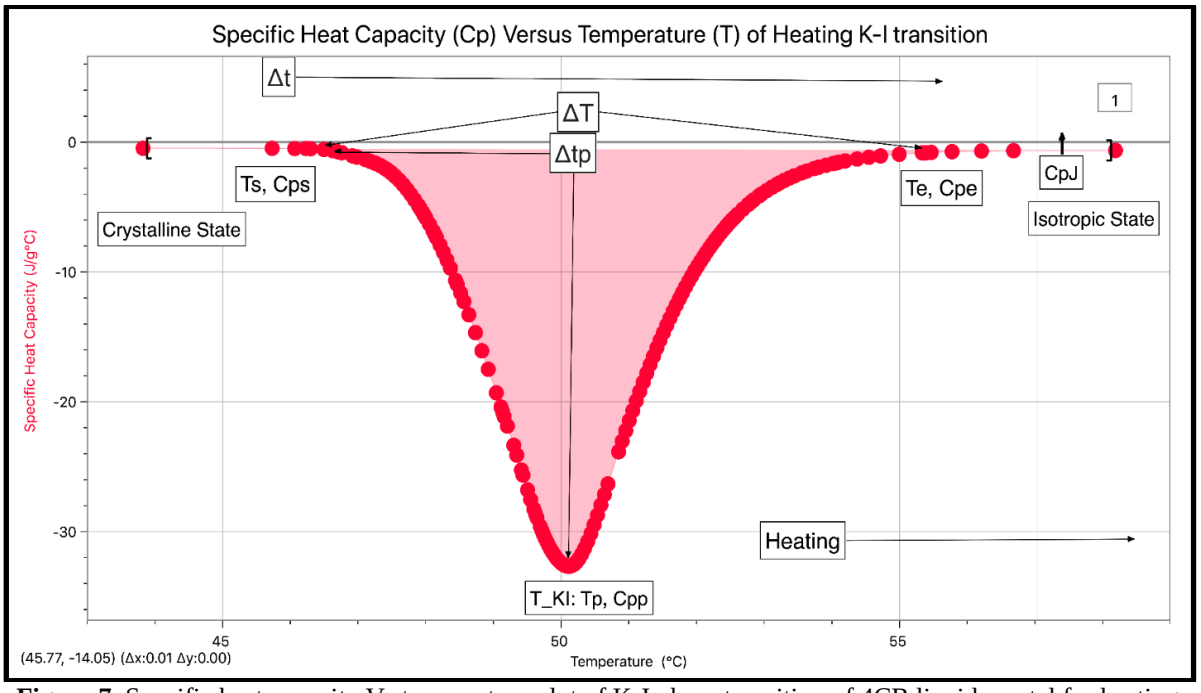

Figure 7. Specific heat capacity Vs temperature plot of K-I phase transition of 4CB liquid crystal for heating. The highlighted red color represents the peak integral of the K-I phase transition; the amount of thermal energy absorbed for the K-I phase transition.

The data details of K-I transition and glass transitions appearing in heating for 4CB can be seen in **Table 1** where the meaning of each symbol is as follows. The T_s, T_e, are the start and end temperatures of the K-I transition. T_{KI} is the peak temperature of K-I transition, ΔT is the temperature range for K-I peak, C_{ps}, C_{pe}, C_{pp}, C_{pj} are the specific heat capacity of the start, end, peak value, and wing jump of the peak. The ΔC_p, is the change in specific heat capacity for K-I peak. The Δt, Δt_p, $\Delta t_{p\%}$ are the time taken by molecules in K-I transition, to reach the peak value of transition and percent change to get the peak value in seconds and ΔH is the enthalpy of the transition. The T_{g1}, T_{g2} are the glass transition temperature in heating for 4CB.

Table 1. Thermodynamic data details for heating of the K-I phase transition.

Heating for K-I													
Sample	T_s (°C)	T_e (°C)	T_{KI} (°C)	ΔT (°C)	C_{ps} (J/g°C)	C_{pe} (J/g°C)	C_{pp} (J/g°C)	C_{pJ} (J/g°C)	ΔC_p (J/g°C)	Δt (s)	Δt_p (s)	$\Delta t_{p\%}$ (s)	ΔH (J/g)
4CB	46.32	55.81	50.11	9.49	0.51	0.71	32.93	0.20	32.44	1.58	0.63	39.9	106.6
T_{g1} (°C) = 10.02			T_{g2} (°C) = 22.18										

Theenthalpies are also found for the I-N phase transition of 4CB in cooling for exothermic peaks as release of thermal energy can be seen in Figure 8.

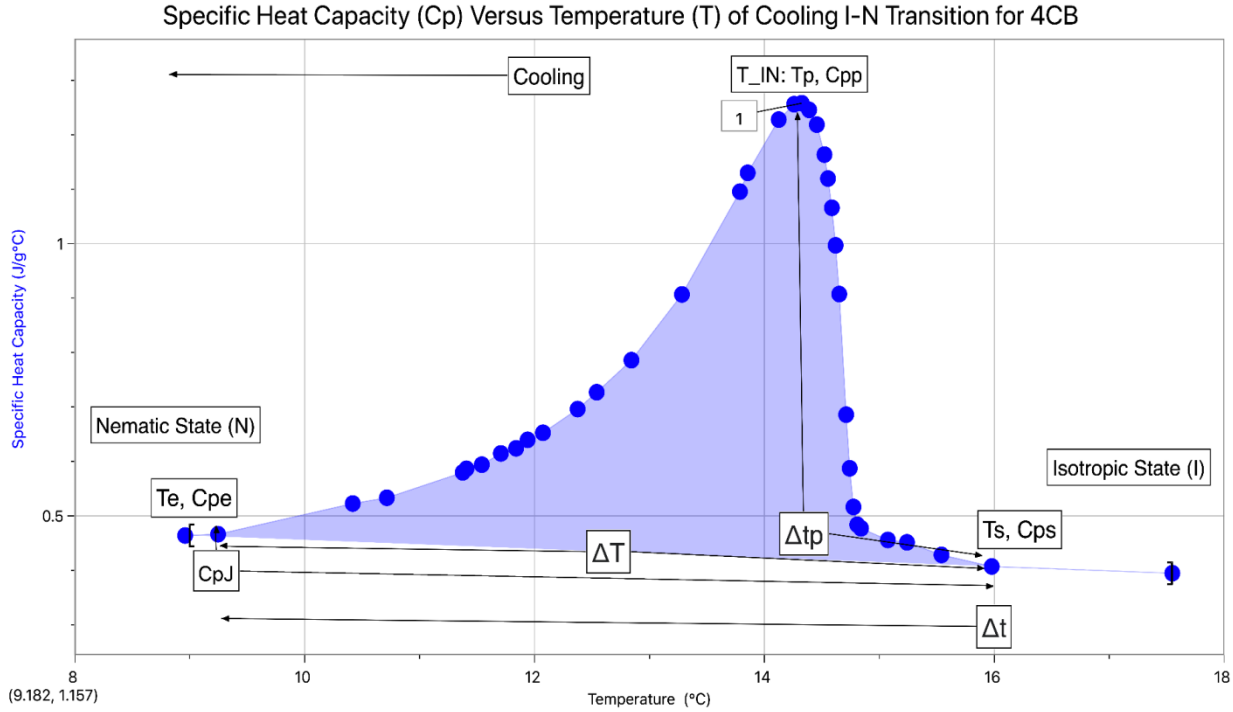

Figure 8. Specific heat capacity Vs temperature of I-N phase transition of 4CB liquid crystal for cooling. The blue highlight represents the peak integral of the I-N phase transition, or the amount of energy absorbed for the I-N phase transition.

The data details of the I-N transition appearing in cooling for 4CB can be seen in **Table 2**where the meaning of each symbol is as same as shown for **Table 1,** but it is for I-N transition only.

Table 2. Thermodynamic data details for cooling of the I-N phase transition.

Cooling for I-N													
Sample	T_s (°C)	T_e (°C)	T_{IN} (°C)	ΔT (°C)	C_{ps} (J/g°C)	C_{pe} (J/g°C)	C_{pp} (J/g°C)	C_{pJ} (J/g°C)	ΔC_p (J/g°C)	Δt (s)	Δt_p (s)	$\Delta t_{p\%}$ (s)	ΔH (J/g)
4CB	15.99	8.97	14.33	7.02	0.41	0.47	1.26	0.06	0.86	1.17	0.28	23.9	9.02

Theenthalpies are also found for the N-K phase transition of 4CB in cooling for exothermic peaks as release of thermal energy can be seen in Figure 9 and data details of N-K transition in cooling can be seen in the **Table 3.**

Table 3. Thermodynamic data details for cooling of the N-K phase transition.

Cooling for N-K												
Sample	T_s (°C)	T_e (°C)	ΔT (°C)	C_{ps} (J/g°C)	C_{pe} (J/g°C)	C_{pp} (J/g°C)	C_{pJ} (J/g°C)	ΔC_p (J/g°C)	Δt (s)	Δt_p (s)	$\Delta t_{p\%}$ (s)	ΔH (J/g)
4CB	-9.98	-17.6	7.62	0.1	0.01	10.35 and 9.08	0.09	10.28	1.27	0.26 and 0.63	20.5 and 49.6	41.07
T_{NK1} (°C) = -11.51					T_{NK2} (°C) = -13.75							

Figure 8 isolates the exothermic I-N phase transition for individual transition peak integration. The shaded area shows the integral of the I-N phase transition being taken to discover how much energy was released to allow this exothermic phase transition to occur during cooling. The energy released to achieve the I-N transition was 9.02 J/g.

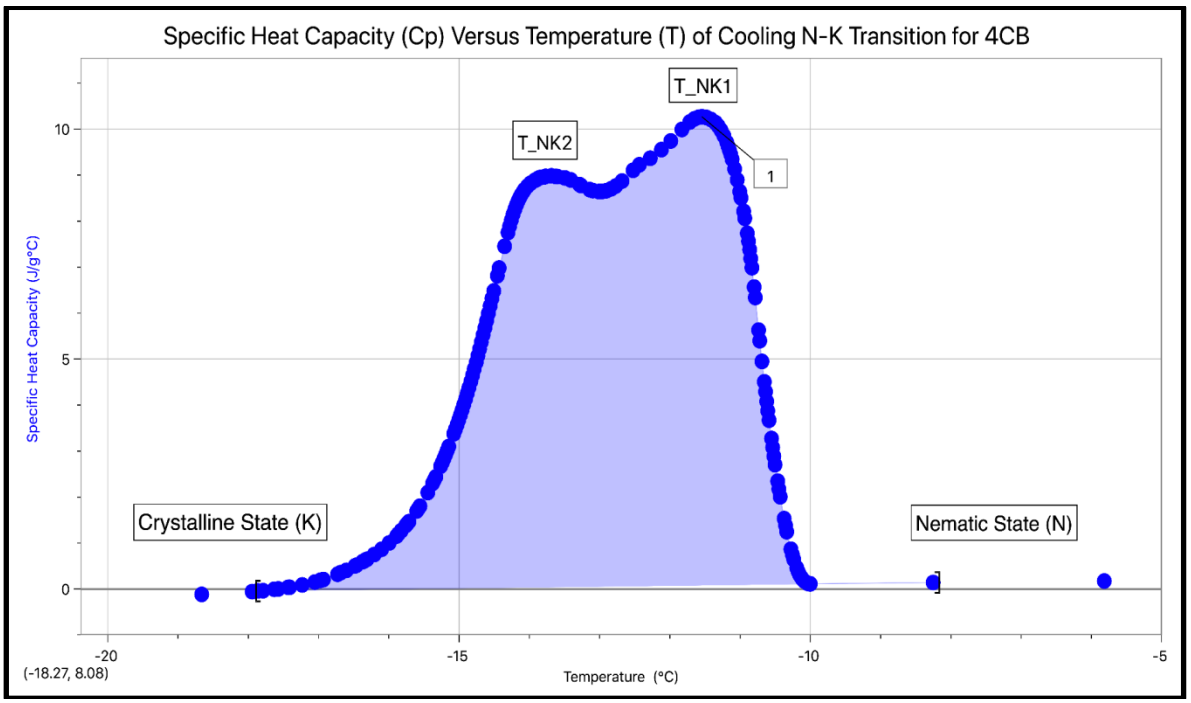

Figure 9. Specific heat capacity Vs temperature of N-K phase transition of 4CB liquid crystal for cooling. The blue highlight represents the peak integral of the N-K phase transition, or the amount of energy absorbed for the N-K phase transition.

Figure 9 shows energy released for N-K transition as 41.07 J/g. The total enthalpy for I-N and N-K can be seen in Figure 10 that shows how much total thermal energy is released during cooling of 4CB.

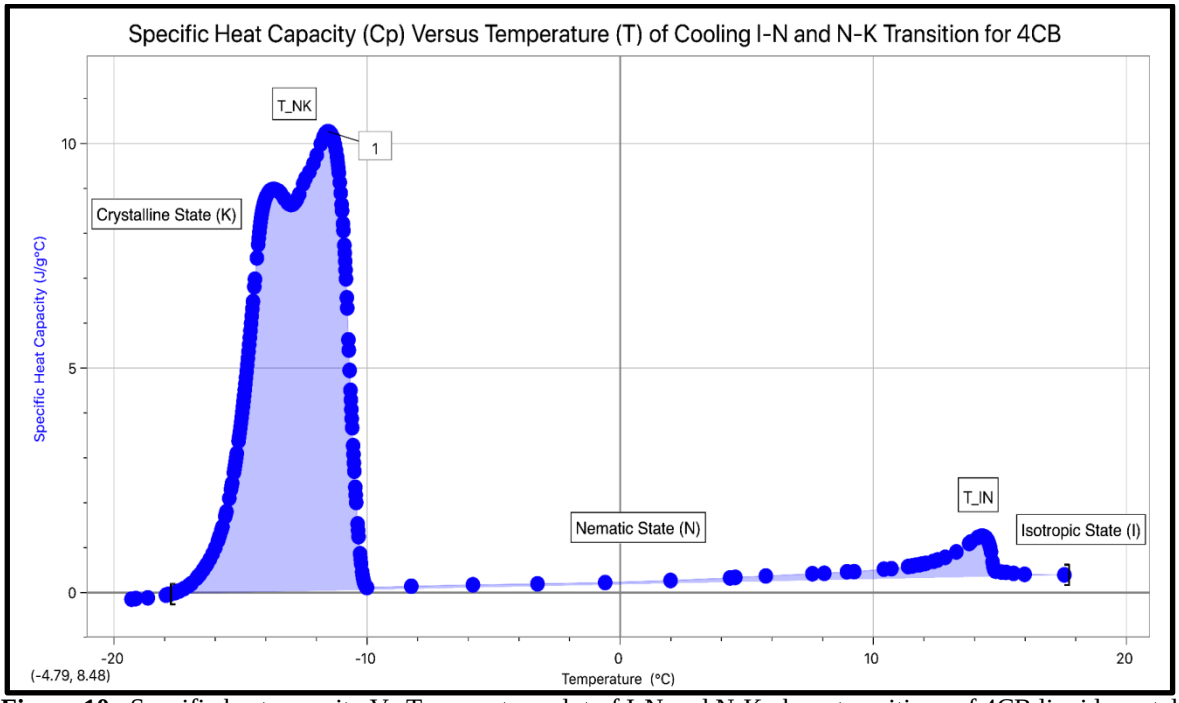

Figure 10. Specific heat capacity Vs Temperature plot of I-N and N-K phase transitions of 4CB liquid crystal for cooling. The blue highlight represents the peak integral of the I-N and N-K phase transitions.

V. DISCUSSION

(a) Comparing 4CB and 6CB behavior

The heating and cooling phase transitions of 4CB highlighted in Figure 3 is compared with the phase transitions of 6CB in Figure 4 and it displays notable differences. First, the 4CB result does not show a nematic phase during the heating scan, it instead shows a large, endothermic, K-I phase transition at 50.10 °C. In 6CB, as seen in Figure 4, it shows crystalline and nematic phases as K-N and N-I phase transition peaks that occur at 16.76 °C and 29.76 °C respectively. It is also noticed in Figure 3 that 4CB shows nematic and crystalline as two cooling phase transition peaks whereas cooling crystallization has two peaks and shows double or multiple crystallization for 4CB. The I-N phase transition peak in 4CB occurs at 14.34 °C whereas the I-N cooling peak occurs at 26.85 °C for 6CB. Lastly, the N-K cooling transition of 4CB occurred in two parts at -11.47 °C and -13.78 °C, whereas the "typical" 6CB cooling N-K phase transition occurred at 0.48 °C. Not only is it noteworthy that 4CB is missing the nematic phase in heating but has a two-part N-K phase transition in cooling, but also that all the 4CB transitions occur over a far wider temperature range. The difference in temperature between the heating K-I transition and final cooling N-K transition of 4CB is 63.88 °C, whereas the temperature difference between the heating N-I and cooling N-K transitions of 6CB is 29.28 °C. The data details can be seen in **Table 4.**

Table 4. Comparing thermodynamics of 4CB and 6CB heating and cooling phase transitions

	Heating					Cooling				
Sample	**T_{KI} (°C)**	**T_{KN} (°C)**	**T_{NI} (°C)**	**ΔH_K (J/g)**	**ΔH_N (J/g)**	**T_{IN} (°C)**	**T_{K1} (°C)**	**T_{K2} (°C)**	**ΔH_K (J/g)**	**ΔH_N (J/g)**
4CB	50.11	N/A	N/A	106.59	N/A	14.33	-11.51	-13.75	41.07	9.02
6CB	N/A	16.76	29.76	70.11	3.24	29.73	0.47	N/A	35.57	1.53

Typically, nCB family members from n = 5 to n = 8 [17] show crystalline, nematic, and isotropic phase transitions when they are heated and cooled. This typical behavior is seen in 6CB too and can be shown as drawing in Figure 11. It can be seen that 6CB molecules are completely organized in crystalline (K) state and then become partially organized in Nematic (N) and then completely disorganized in Isotropic (I) state; either 6CB is heated or cooled.

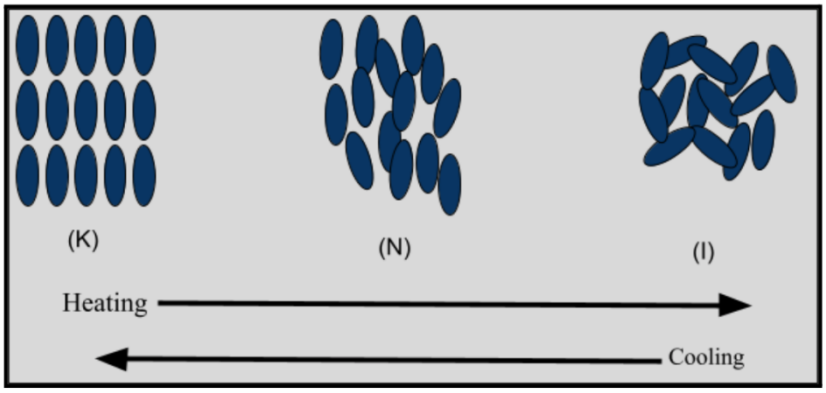

Figure 11. The molecular alignment of 6CB in Crystalline (K), Nematic (N) and Isotropic (I) states in heating and cooling.

But when 4 CB is heated, it starts from Crystalline (K) to Glassy state # 1 (G1) and then goes to Glassy state # 2 (G2) and then go to Isotropic (I). The molecular arrangement and alignment in these states for 4CB can be seen as drawing in Figure 12.

It can be seen that 4CB molecules are arranged completely in ordered shape in K and then some of the molecules lost their organization and become completely unorganized when they are heated and go to G1 state and then when heating is continued, the molecules go to G2 by showing decreased organization but still stays in solid state, then molecules go to liquid state and becomes completely disorganized in I state.

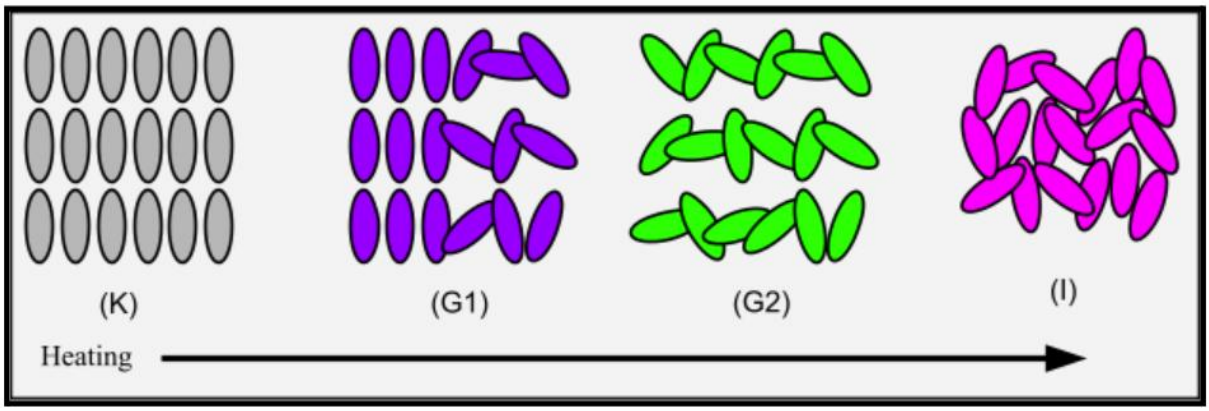

Figure 12. The molecular arrangement of 4CB liquid crystal in Crystalline (K), Glass transition #1(G1), Glass transition # 2(G2) and Isotropic (I) for the heating.

On the other hand, when 4CB is cooled, it follows I to N and then N to K transitions where it shows double crystallization. Which can be seen in the drawing shown as Figure 13 where 4CB follows Isotropic state as liquid state when it was in melt condition and completely disorganized but then when 4CB is cooled, it shows partial alignment and goes into Nematic state and then follows more organized state in two steps as double crystallization as K1 and K2.

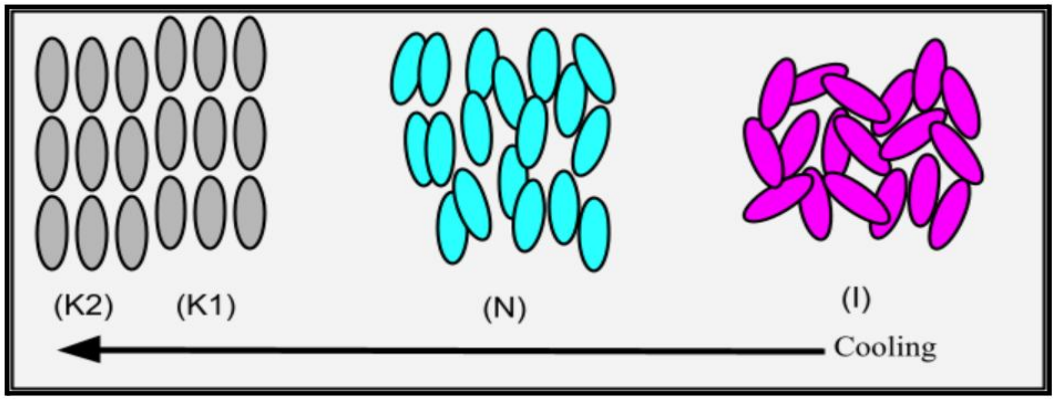

Figure 13. The molecular arrangement of 4CB liquid crystals in cooling follows the order from Isotropic (I) to Nematic (N) to Double Crystallization (K1, K2).

(b) Heating Vs Cooling of 4CB

As seen in Figure 8 for the integration of the heating and cooling phase transitions of 4CB, the single K-I heating transition is much larger than both the I-N and N-K phase transition peaks. Considering the integral value as representation of the total internal energy change of the system during the heating and cooling process, 225.1 J/g represented graphically as a negative quantity suggests that far more energy was absorbed during the endothermic process than was released during the exothermic process, giving an overall increase in internal energy of the 4CB system.

The energy absorbed during heating through K-I phase transition of 4CB is found as 106.6 J/g that shows that 4CB molecules take this much energy which is larger than required and hence they skip nematic phase and jump to the isotropic phase in heating. The peak integral for the cooling I-N phase transition was 9.02 J/g, and the cooling N-K phase transition peak integral was 41.07 J/g, as seen in **Tables 1, 2 and 2 shows the release of energy during cooling that make 4CB molecules slow down and hence they gets enough time to arrange themself in nematic state and then go to multiple crystallization.** Adding the integrals for both the cooling phase transition peaks only gives 50.09 J/g for the entire cooling scan which is smaller than the amount of energy 4CB molecules take while heating. The single heating K-I transition is over double that value, suggesting that far more energy was absorbed during the heating process than was released during the cooling process and hence show double crystallization.

(c) Double Crystallization as Cooling N-K Transition

As seen in Figures 9 and 10,the two peaks of the N-K cooling phase transition of 4CB represent a unique double crystallization. It is suspected that the small molecular size with small tail of 4CB LC allows its molecules to become tightly packed upon cooling, but not oriented in a fully crystalline solid state. Only when more heat is released are the LC molecules able to shift again into their lower energy, more favorable crystalline state. As seen in Table 3, there are two values for the T_{NK} = -11.51 °C / -13.75 °C, the C_{pp} = 10.35 J/g°C / 9.08 J/g°C, and the Δt_p = 0.26 s / 0.63 s, because of this twostep cooling transition. As seen in the zoomed in Figure 6, the double glass transition observed before the heating K-I phase transition peak is seen as a twostep process like the double crystallization observed in the cooling of 4CB. The first glass transition occurred at T_{g1} = 10.02 °C and the second glass transition at T_{g2} = 22.18°C. The two stepped glass transition in heating provides potential insight on why 4CB displays a double crystallization in cooling.

(d) Comparing Heating of 4CB and 6CB

Comparing differences in the heating scans of 4CB and 6CB brings attention to the absence of the nematic state in the heating scan of 4CB as shown in Figure 14. Heating 6CB not only presents the nematic transition but shows a wider K-N transition peak than 4CB's K-I transition peak. This means between 4CB and 6CB, it takes more of a temperature change (ΔT) and more time (Δt) for 6CB to do its K-N then K-I transitions than 4CB to do just its K-I transition. 4CB's K-I transition peak is narrower than 6CB's K-N peak but occurs at a higher temperature. So 4CB has a much quicker transition to isotropic state than 6CB but requires more energy. The specific heat capacity values would produce a much larger wing jump in 6CB than 4CB's K-I transition that indicates that 4CB energy level is lower than 6CB and needs more energy to go through the transitions.

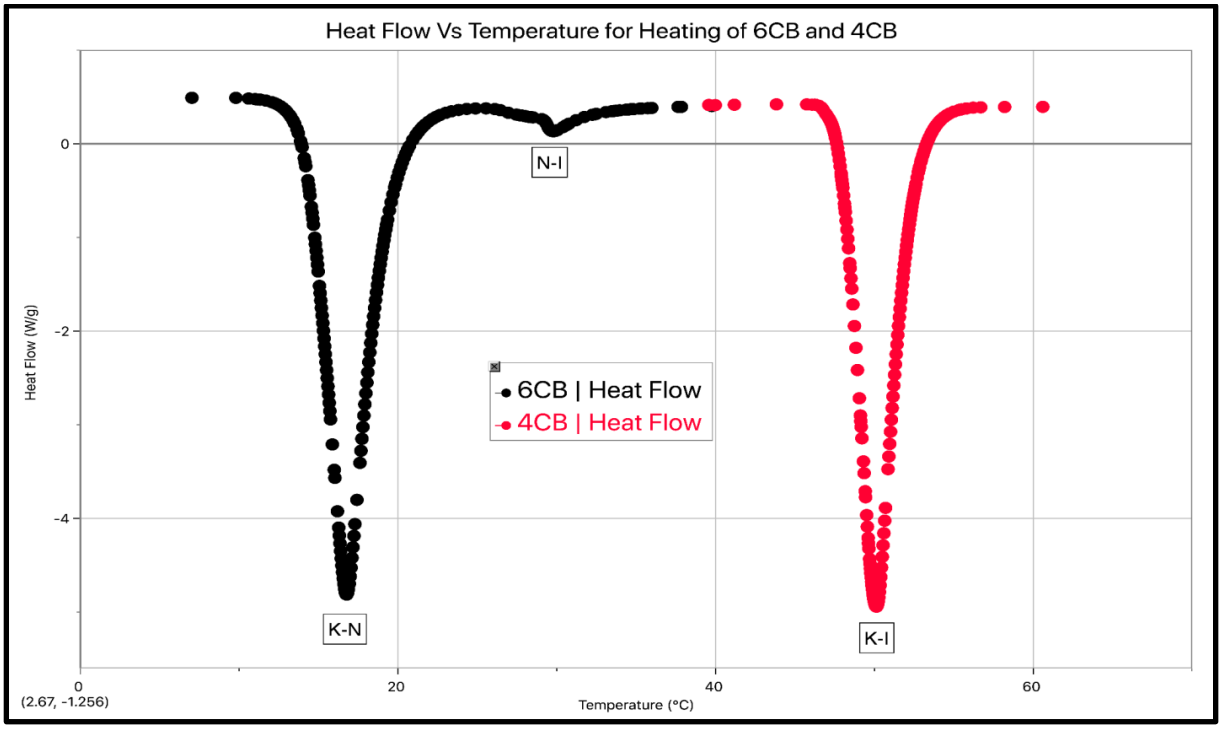

Figure 14. Heat flow Vs Temperature data comparison between the heating phase transitions of 4CB and 6CB.

(e) Comparison of 4CB + 6CB

Being the smallest member of the nCB liquid crystal family, the 4CB is the first liquid crystal in nCB, it has the smallest tail of the carbon chain compared to 6CB. Based on a detailed study of 4CB as explained above, it is completely clear that 4CB shows two unique properties in heating and two unique properties in cooling that 6CB doesn't show and as well as the other bigger members of the nCB family do not show either. Briefly summarizing this uniqueness of 4CB once again here is that 4CB shows 1) the presence of two glass transition temperatures at heating as G1 and G2, 2) shows absence of nematic state in heating, 3) shows the presence of nematic in cooling, 4) shows double crystallization in the cooling after nematic state when it is cooled from isotropic to crystallization. These four strange behaviors of 4CB makes it unique in the nCB liquid crystal family and make 4CB very different from 6CB liquid crystal.

This strange behavior of 4CB can be explained in terms of spring theory. The C-C, C=C, C-H and C☰N bonds behave like springs. [16] The bonds in Benzene rings and Cyano groups are more packed and bound, hence have less freedom to move and behave like a very stiff spring. Whereas the C-C and C-H bonds that are in the tail of 4CB and 6CB have more freedom to move. As seen in Figure 15 the 3D drawing depicting the molecules of 6CB and 4CB with six green carbons and Four carbons in the tail of 6CB and 4CB can be considered as attached with each other with springs.

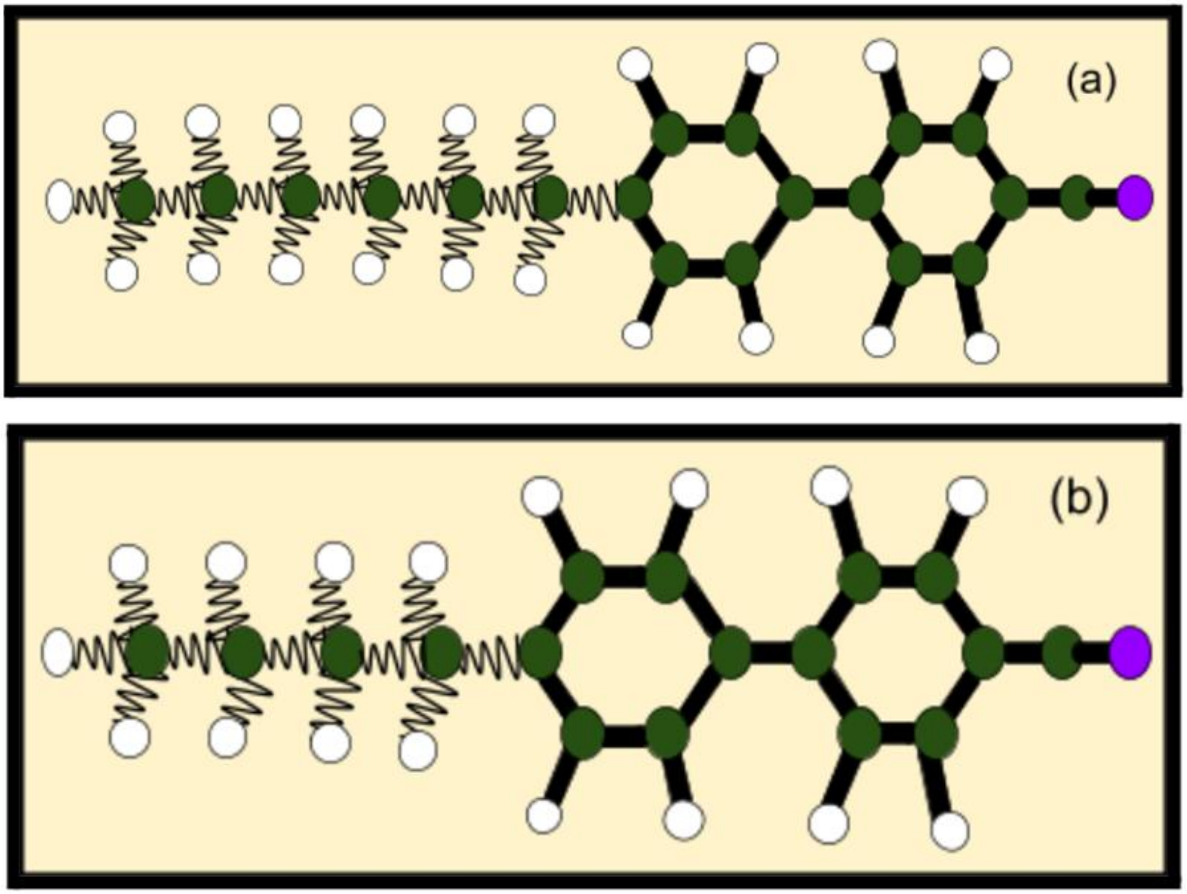

Figure 15. The C-C and C-H tail formed with Carbon (Green), Hydrogen (White) in (a) 6CB and (b) 4CB liquid crystals showing spring-like structure in liquid crystal.

When molecules of 6CB and 4CB move, these springs stretch and compress. These springs follow Hooke's Law as mentioned in the equation # 4a in the theory section. As the force applied (F) by Carbon atoms increases, the extension between them (x) increases. Since 6CB has Six carbon atoms in the tail, these carbon atoms applied more force as net force and hence the extension in 6CB is more than 4CB and hence 6CB moves flexibly whereas 4CB does not. The spring constant of C-C and C-H bonds are $4.5*10^{-5}$ N/cm and $5.2*10^{-5}$ N/cm respectively. [16]

Detailed explanation of the spring theory can be seen in Figure 16. This Figure shows a model of springs where when four carbons are attached with their single bonds in the tail of 4CB, they can be considered as four springs in series whereas when six carbons are attached to the single bond in the tail of 6CB, they can be considered as six springs attached in series. Following theory of springs in series as shown in the equation # 4c in the theory section, as the number of carbon atoms increases, the total spring constant decreases and makes the model more flexible.

Following equation # 4c, the total spring constant of the tail of 4CB will be k/4 whereas for 6CB will have k/6. If further, the theory of elastic potential energy is followed as shown in the equation # 4b, the U_e for 4CB will be more than 6CB. The spring theory and model indicates that having stiffer bonds and a shorter tail requires 4CB to absorb higher thermal energy while it is heated, and the stiffer spring stores higher potential energy which makes 4CB move quickly from Crystalline to Glassy, then to Isotropic state by skipping Nematic state. Whereas 6CB shows more flexibility and hence stores less elastic potential energy, which is why it takes time to change transitions and get enough time to go to Nematic state after crystallization in heating. On cooling, the tail of 6CB maintains its flexibility and goes to the same phases in cooling as well, whereas 4CB gets flexible at hottest temperature because of heat, so when it is cooled it loses its flexibility and hence shows Nematic state in cooling but then also shows two step crystallization as double crystallization.

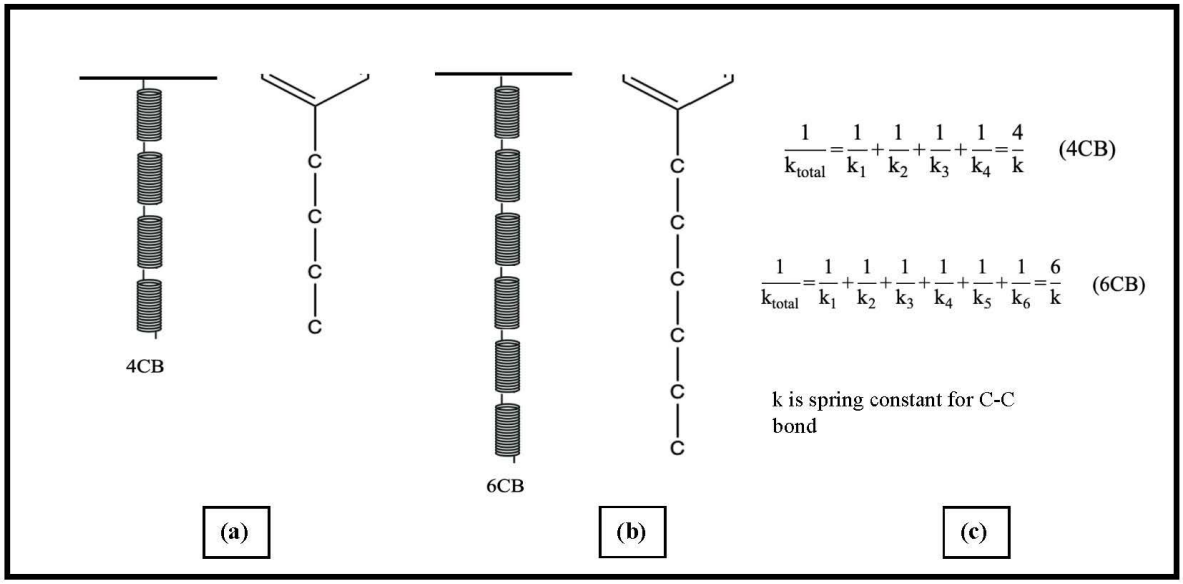

Figure 16. A model depicting the structure of C-C bonds in **(a)** 4CB and **(b)** 6CB showing **(c)** spring theory as a combination of springs in series. All ks are the same and equal.

VI. CONCLUSION

The purpose of this research is to find details of the 4-Butyl-4-Cyanobiphenyl (4CB) liquid crystal and understand its unique behavior by analyzing its Differential Scanning Calorimetric (DSC) data using Logger Pro data analysis software. To understand the strange behavior of 4CB, the 4CB was compared to its next even member of the Alkyl Cyanobiphenyl family member of 4-Hexyl-Cyanobiphenyl (6CB) liquid crystal. When the 4CB and 6CB liquid crystals are compared, it is found that 4CB shows two unique things in its heating and two unique things in its cooling. It is found that 4CB shows two glass transitions (G1, G2) and then melting transition (K-I) on heating. The 4CB doesn't show the presence of a Nematic state in heating. Whereas 4CB shows the presence of Nematic state in cooling after Isotropic state and then it shows double crystallization instead of single crystallization in cooling. These details of 4CB makes this research significant as no report is found on literature on this type of study so far.

The 4CB shows two glass transitions T_{g1} = 10.02 °C and T_{g2} = 22.18 °C in heating and shows two crystallizations at T_{NK1} = -11.51 °C and T_{NK2} = -13.75 °C in cooling. The 4CB shows Nematic transition at 14.34 °C on cooling but not in heating. These results expand the knowledge and information about 4CB in the literature about its unexpected thermodynamic behavior which can further be used in real world applications such as in Liquid Crystal Displays (LCDs). Modern research on LCDs supports the use of LC that have the Nematic state, which 4CB displays only during the cooling but not in heating. The 4CB shows K-I at higher temperature on heating compared to 6CB, but the cooling I-N transition occurs at a much lower temperature than 6CB. Although 4CB does not show the nematic state in the heating like 6CB does, it does in its cooling at a much more favorable temperature. This strange behavior of 4CB could validate it to be used in LCDs to prevent the common LCD issue of not working in extreme cold temperature conditions, even a little below freezing, due to the significant supercooling effect during wintertime as observed in the DSC of 4CB.

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REFERENCES

[1]. *Liquid Crystal Displays*. Liquid Crystals. (n.d.). Retrieved February 24, 2022, from https://www.ch.ic.ac.uk/local/projects/abbott/LCDs.htm

[2]. Dunmur, D., & Walton, H. G. (n.d.). *Projection displays*. Encyclopædia Britannica. Retrieved March 4, 2022, from https://www.britannica.com/technology/liquid-crystal-display/Projection-displays.

[3]. Sharma, D. (2010). Non-isothermal kinetics of melting and nematic to isotropic phase transitions of 5CB liquid crystal. *Journal of Thermal Analysis and Calorimetry*, *102*(2), 627–632.

[4]. Sharma D, MacDonald J, Iannacchione G. Thermodynamics of Activated Phase Transitions of 8CB: DSC and MC Calorimetry. J Phys Chem B. 2006; 110: 16679-16684.

[5]. *What are liquid crystals?* Kent State University. (n.d.). Retrieved March 4, 2022, from http://www.kent.edu/amlci/what-are-liquid-crystals
[6]. *Nematic vs Smectic Phase in LCDs - Nelson-Miller, Inc.* Nelson Miller. (2021, May 15). Retrieved March 4, 2022, from http://www.nelson-miller.com/nematic-vs-smectic-phase-in-lcds/
[7]. Sharma, D., MacDonald, J. C., Shukla, R. K., & Kumar, A. (2016). Existence of three activation energies in the melting transition of SeInAg glassy alloy. *Trends in Physical Chemistry*, *16*, 87–94.
[8]. Sharma, D. (2008). Kinetics of nanocolloids in the aligned domain of octylcyanobiphenyl and Aerosil Dispersion. *Liquid Crystals*, *35*(10), 1215–1224.
[9]. Haines PJ, Reading, M, Wilburn FW. Differential thermal analysis and differential scanning calorimetry. In Brown ME (ed): Handbook of Thermal Analysis and Calorimetry, vol 1. The Netherlands: Elsevier Science BV, 1998;279–361.
[10]. Danley RL. New heat flux DSC measurement technique. Thermochim Acta 2002; 395:201–208.
[11]. Haines PJ, Reading, M, Wilburn FW. Differential thermal analysis and differential scanning calorimetry. In Brown ME (ed): Handbook of Thermal Analysis and Calorimetry, vol 1. The Netherlands: Elsevier Science BV, 1998;279–361.
[12]. *Differential scanning calorimetry - how does it work?*LinseisMessgeräte GmbH. (2020, November 26). Retrieved March 4, 2022, from https://www.linseis.com/en/methods/differential-scanning-calorimetry-dsc/
[13]. Sharma, D. (2008). Calorimetric study of activated kinetics of the nematic and smectic phase transitions in an aligned nano-colloidal liquid crystal+aerosil gel. *Journal of Thermal Analysis and Calorimetry*, *93*(3), 899–906.
[14]. McDonough, K., Chau Vy, Ngoc, & Sharma, D. (2014). Existence of time lag in crystalline to smectic A (K–SMA) phase transition of 4-decyl-4-biphenylcarbonitrile (10CB) liquid crystal. *Journal of Thermal Analysis and Calorimetry*, *116*(3), 1515–1520.
[15]. Netzsch. (n.d.). *Glass transition temperature*. Analyzing & Testing. Retrieved April 14, 2022, from https://analyzing-testing.netzsch.com/en-US/training-know-how/glossary/glass-transition-temperature#:~:text=In%20DSC%20measurements%2C%20the%20glass,J%2F(g%E2%8B%85K)
[16]. Robinson, E. A., Lister, M. W., E. A. RobinsonView all articles by this author, & M. W. ListerView all articles by this author. (1963, December 1). A linear relationship between Bond orders and stretching force constants. Canadian Journal of Chemistry. Retrieved from https://cdnsciencepub.com/doi/full/10.1139/v63-439